The Minimum Electron Energies Associated with the Excitation of the Spectra of Helium.

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[Plate 13.]

Introduction.

In addition to the orthohelium and parhelium serial systems, the spectrum of helium includes the lines of the enhanced system and the many-lined, or band, spectrum. The lines of the orthohelium and parhelium series are attributed to transitions of electrons within uncharged helium atoms, while the enhanced lines are attributed to the transitions of the remaining electrons in already ionised helium atoms. It has been suggested that the band spectrum of helium arises from disturbances of helium molecules (He_2), for the formation of which electrical excitation is postulated as a preliminary condition.*

On the view that each of the lines of the orthohelium and parhelium series corresponds to a definite transition of one of the electrons in the normal helium atom, it might be expected that it would be possible to excite certain of the series lines without exciting others by suitably adjusting the disturbing force, so as to make the occurrence of certain transitions impossible. The investigations of Rau,† of Horton and Bailey,‡ and of Compton and Lilly,§ have led to the conclusion that it is not possible to excite certain of the orthohelium and parhelium series lines without exciting all of them. This conclusion is in complete agreement with the work of McLennan and Ireton,‖ and of Foote and Meggers,¶ on the spectra of metallic vapours. These investigators found that the only lines which could be excited without all the lines appearing were the first lines of the series whose limiting frequencies corresponded to the respective ionisation potential differences of the metallic vapours concerned, a result which was supported by the current-potential difference curves of Tate and Foote,* and of Mohler, Foote and Meggers,† etc. These observers found that the only types of inelastic impacts, which occurred between atoms of the metallic vapours and electrons, were those corresponding to the ionisation of the atom, and to the voltages which were connected by the quantum relation with the frequencies of the first lines of the series whose limits were connected with the ionisation potential differences. The lines of the helium spectrum which, by analogy with the cases of the metallic vapours, might be expected to appear before the other helium lines, are in the extreme ultra-violet region of the spectrum, and could only be detected with a vacuum grating spectroscope‡: this was not used by either of the investigators to whose work in helium reference has been made.

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* W. Lenz, 'Deutsch. Phys. Ges. Verh.,' vol. 21, p. 632 (1919), and A. Sommerfeld, 'Atombau und Spektrallinien,' p. 563.

† H. Rau, 'Würzburg Phys. Med. Ges. Ber.,' February, 1914.

‡ F. Horton and D. Bailey, 'Brit. Ass. Reports,' 1919, p. 153.

§ K. T. Compton and E. G. Lilly, 'Astro.-Phys. Journal,' vol. 52, p. 1 (1920).

‖ J. C. McLennan and H. J. C. Ireton, 'Phil. Mag.,' vol. 36, p. 450 (1918).

¶ P. D. Foote and W. F. Meggers, 'Phil. Mag.,' vol. 40, p. 80 (1920).

A different result was obtained by Richardson and Bazzoni,§ who came to the conclusion that a genuine difference of about 0·5 volt existed in the energies required for the excitation of λ 4472 and λ 5876, and a difference of 0·25 volt between the energies required for λ 4713 and λ 5876, the latter line appearing at the lower voltage in each case.

In a recent research by Franck and Knipping‖ on the potentials of excitation of helium, these experimenters have obtained a series of bends in their current-potential difference curves at voltages intermediate to the minimum voltage for inelastic impact and the minimum ionisation voltage. These bends are interpreted as indicating the excitation of different ultra-violet series lines, one by one, as the corresponding electron energy is acquired. This would mean that at each bend in the curve a new set of interorbital transitions became included in the transitions possible for the given value of the exciting electron energy, and it therefore suggests that different amounts of energy are required for the excitation of different lines in the orthohelium and parhelium series. Franck and Knipping's interpretation of the bends in their curves involves the acceptance of certain views with regard to the particular electron transitions which give rise to the orthohelium and the parhelium series lines, and, on the basis of these views, the order of appearance of the different lines for increasing values of the voltage, and the particular values of the potential differences at which certain lines should be excited, can be calculated.

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* J. Tate and P. D. Foote, 'Phil. Mag.,' vol. 36, p. 64 (1918).

† F. L. Mohler, P. D. Foote, and W. F. Meggers, 'Bur. Stan.,' 1920, p. 734.

‡ It has been shown (Horton and Davies, 'Phil. Mag.,' vol. 42, p. 746, 1921), that the radiations which are emitted at the two critical radiation voltages found in helium can be absorbed and re-emitted by other helium atoms. This effect would result in a "scattering" of these radiations in a vacuum grating spectroscope, and might prevent them from being detected, thus accounting for the fact that, in his earlier researches on the extreme ultra-violet spectrum of helium, Lyman obtained no trace of lines corresponding to these critical voltages. It therefore seems probable that the line at λ 585 (the wave-length corresponding to the higher critical radiation voltage in helium), recently detected by Fricke and Lyman ('Phil. Mag.,' vol. 41, p. 814, 1921) does not originate from the helium itself. The fact that no line was detected at the wave-length corresponding to the lower critical radiation voltage supports this suggestion.

§ O. W. Richardson and C. B. Bazzoni, 'Nature,' vol. 98, p. 5 (1917).

‖ J. Franck and P. Knipping, 'Zeits. f. Phys.,' vol. 1, p. 320 (1920).

The views referred to are that the orthohelium and parhelium principal series are concerned with transitions involving a return of the displaced electron within a helium atom to the orbits to which electrons are removed at the first and second, respectively, of the critical voltages at which photoelectrically active radiations have been detected in the current-voltage curves. Investigations of the production of radiation and of ionisation in helium have shown that the minimum radiation potential difference is 20·4 volts and that the minimum ionisation potential difference is 25·2 volts. The difference between these two critical voltages is 4·8 volts, a value which is in good agreement with the voltage 4·78 connected by the quantum relation with the limiting frequency of the orthohelium principal series. It therefore seems reasonable to associate this series with the orbit to which an electron within a helium atom is removed as the result of an inelastic impact with an electron having 20·4 volts energy. The second critical radiation voltage, 21·2 volts, was not detected until its existence had been foreshadowed from theoretical considerations by Landé,* who attributed the existence of two independent serial systems in the helium spectrum to the existence of two independent sets of outer orbits. According to Landé, one of these sets of outer orbits, namely, the set of orbits associated with the orthohelium series, is coplanar with the orbit of the undisturbed electron, while the plane of the set of orbits associated with the parhelium serial system is at angle with the plane of this orbit. The limiting frequencies of the orthohelium and parhelium principal series are connected by the quantum relation with the voltages 4·78 and 3·98 respectively, so that the energy required to remove an electron in a normal helium atom to the orbit from which the parhelium principal series originates must be (4·78 − 3·98 =) 0·8 volt higher than 20·4 volts. The existence of a second radiation voltage at 21·2 volts has been found experimentally by Franck and Knipping,† and by Horton and Davies.‡ In their more recent paper, Franck and Knipping describe experiments from which they conclude that though inelastic collisions occur when electrons with 20·4 volts energy collide with helium atoms, such collisions are not followed by an emission of radiation unless there is impurity present in the helium. These conclusions confirm Franck and Reiche's suggestion* that the abnormal coplanar helium atoms, which result from 20·4-volts impacts, are "metastable," a suggestion which follows from their hypothesis that the normal state of the helium atom is identical with the unit quantum sharp series state of the crossed system of orbits. This hypothesis has been criticised on theoretical grounds by Kemble,† while the conclusions drawn by Franck and Knipping have been criticised by Horton and Davies.

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* A. Landé, 'Phys. Zeits.,' vol. 20, p. 228 (1919).

† J. Franck and P. Knipping, 'Phys. Zeits.,' vol. 20, p. 481 (1919).

‡ F. Horton and A. C. Davies, 'Phil. Mag.,' vol. 42, p. 746 (1921).

Franck and Knipping have identified the bends in their curves in helium, intermediate to the radiation voltage 21·2 and the ionisation voltage, with the excitation of successive lines of an ultra-violet series whose first term corresponds to 21·2 volts, and whose last term corresponds to the ionisation voltage, because by adding to 21·2 volts the potential differences corresponding to the successive terms of the parhelium principal series, *i.e.*, the series originating from the 21·2-volts orbit, they obtained good agreement between the calculated values of the potential differences corresponding to the excitation of successive lines of this ultra-violet series, and the potential differences at which the bends occurred. The absence of bends at the voltages obtained by adding to 20·4 volts the potential differences corresponding to the successive frequencies of the orthohelium principal series lines, is interpreted by Franck and Knipping as being due to the fact that, except in special circumstances, transitions between the crossed and coplanar systems cannot occur. When displacements to the coplanar system of orbits have occurred, the electrons are supposed to return to the 20·4-volts orbit (not to the normal orbit), so that the resulting lines of the orthohelium system would be of too long a wave-length to produce photoelectrons and so to give an indication in the curves.

The minimum voltages at which certain lines of the orthohelium and parhelium series might be expected to appear, if direct transitions from the normal orbit to the orbit from which the electron has to fall to give rise to the particular line in question were possible in each case, have been calculated on the view that these systems are associated with the 20·4 volts orbit and the 21·2 volts orbit respectively. These values are given in Table I. The letters S, P, D, are used in designating terms of the sharp, principal, and diffuse series of parhelium, and the letters *s*, *p*, *d*, for the corresponding series of orthohelium. Table II gives the voltages which have been calculated in the case of some of the lines, on the assumption that direct displacements from the normal orbit, other than those occurring at 20·4 volts and 21·2 volts, can only take place to principal series orbits, as is suggested by the positions of the discontinuities in Franck and Knipping's curves, but that there is no limitation of the possible transitions as the displaced electron returns to the normal orbit. According to Table I, a difference of 0·7 volt should exist between the voltages at which λ 5876 and λ 4472 appear. This is a little higher than the difference recorded by Richardson and Bazzoni. According to the same Table the difference between the voltages at which λ 5876 and λ 4713 should appear is 0·6 volt, which is more than double the difference recorded for these two lines by the above experimenters. Table II, on the other hand, which is based on an assumption for which there appears to be more justification, gives differences which are smaller than those recorded by these observers. The two pieces of evidence in favour of the view that the different lines of the orthohelium and parhelium series can be excited at different voltages are thus not in agreement with one another.

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* J. Franck and O. Reiche, 'Zeits. f. Phys.,' vol. 1, p. 54 (1920).

† E. C. Kemble, 'Phil. Mag.,' vol. 42, p. 123 (1921).

Table I.

Wave-length.	Series.	Exciting voltage.	Wave-length.	Series.	Exciting voltage.
7066	2, $p-m$, s	23·3	4922	2, $P-m$, D	24·3
7282	2, $P-m$, S	23·5	3965	2, $S-m$, P	24·3
3889	2, $s-m$, p	23·6	4438	2, $P-m$, S	24·6
5876	2, $p-m$, d	23·6	4026	2, $p-m$, d	24·6
6678	2, $P-m$, D	23·7	4388	2, $P-m$, D	24·6
5016	2, $S-m$, P	23·7	4121	2, $p-m$, s	24·6
4713	2, $p-m$, s	24·2	4169	2, $P-m$, S	24·8
5048	2, $P-m$, S	24·3	4144	2, $P-m$, D	24·8
3188	2, $s-m$, p	24·3	4024	2, $P-m$, S	24·9
4472	2, $p-m$, d	24·3			

Table II.

Wave-length.	Series.	Exciting voltage.	Wave-length.	Series.	Exciting voltage.
3889	2, $s-m$, p	23·6	3188	2, $s-m$, p	24·3
7066	2, $p-m$, s		5876	2, $p-m$, d	
			4713	2, $p-m$, s	
			3965	2, $S-m$, P	24·3
5016	2, $S-m$, P	23·7	4922	2, $P-m$, D	
6678	2, $P-m$, D		5048	2, $P-m$, S	
7282	2, $P-m$, S		4472	2, $p-m$, d	24·6

In addition to the critical voltages already mentioned, it has been shown, both by Franck and Knipping,* and by Horton and Davies,† that there is another critical value at about 80 volts, at which point further ionisation of helium takes place. The increased production of ionisation is attributed to the removal simultaneously of both electrons from the helium atom. Horton and Davies have further shown that when an intense bombarding electron stream is employed, there is an increased production of ionisation at 55 volts, due to the removal of the second electron from helium atoms which have already been ionised by previous collisions. This value is in fair agreement with the value 54·2 volts calculated from Bohr's theory as the energy required to ionise a positively charged helium atom. It would therefore be expected that under suitable conditions the enhanced lines of helium would make their appearance at these critical voltages. The frequencies of these lines are given by Bohr's equation $\nu = 4\,\mathrm{N}\,(1/n^2-1/m^2)$. The most easily observed of them is λ 4686, the first line of the Fowler series, given by $\nu = 4\,\mathrm{N}\,(1/3^2)-1/m^2)$, where m may have any value from 4 to infinity. Rau (*loc. cit.*) obtained evidence that the line λ 4686 was produced at 80 volts but not at 75 volts. In a paper published while the prevent investigation was in progress, Compton, Lilly, and Olmstead,* record the observation of this line as low as 55 volts, but never below this value, and they found that its intensity was much increased above 80 volts.

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* 'Phys. Zeits.,' vol. 20, p. 481 (1919).

† F. Horton and A. C. Davies, 'Phil. Mag.,' vol. 39, p. 592 (1920).

As the frequency of the line λ 4686 is given by the equation

$$\nu = 4\,\mathrm{N}(1/3^2-1/4^2),$$

the atom will be in a condition to emit the line when the second electron in an ionised helium atom is displaced to orbit 4. Thus an electron would have to acquire the energy corresponding to a potential difference V, given by $\mathrm{V} = h/e\,.\,4\,\mathrm{N}\,(1/1^2-1/4^2)$, or 50·8 volts, in order to be able to excite λ 4686 on collision with a positively charged helium atom.

It has been mentioned earlier that the view has been expressed by Lenz and by Sommerfeld that the band spectrum of helium arises from disturbances of helium molecules formed by the combination of pairs of electrically excited helium atoms. Franck and Knipping have suggested that the particular type of abnormal helium atom concerned is the abnormal coplanar atom resulting from the 20·4 volts electronic-atomic impacts. These abnormal atoms are held by Franck and Knipping to be "metastable," *i.e.*, they cannot revert to the normal state without first undergoing ionisation, or under the influence of strong electric fields, such as would be generated by the formation of short-lived chemical combinations between the metastable helium atoms and atoms of any impurity present in the gas. In the absence of impurities, these abnormal atoms may either remain in the abnormal state or form He_2

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* K. T. Compton, E. G. Lilly, and P. S. Olmstead, 'Phys. Rev.,' vol. 16, p. 282 (1920).

molecules. According to Franck and Knipping, the forces generated at the formation of He_2 molecules are not sufficiently strong to enable the displaced electrons to return to their normal orbits. Horton and Davies have recently shown* that the radiation which is produced as the result of 21·2-volts electron collisions ionises some systems which result from the 20·4-volts collisions. These systems are presumably abnormal atoms or helium molecules.

The following experiments were therefore made to determine the minimum voltages at which lines of the ordinary serial systems, lines of the enhanced system, and lines of the band spectrum, of helium could be obtained under different conditions of gas pressure and electron current density, with a view to testing whether the association of the band spectrum with the He_2 molecule can be reconciled with the recent suggestions as to the production of this molecule, and also with a view to testing the possibility of the excitation of lines in the helium spectrum, other than the single line, without ionisation occurring.

Description of Apparatus, etc.

Two forms of apparatus were used to investigate the excitation of the helium spectrum, one of which was designed with a view to detecting differences in the voltages required for the stimulation of different lines, and the other with a view to obtaining low voltage arcs. One of these forms of apparatus is shown in fig. 1, which is a section at right angles to the lengths of the filaments. In its main features this apparatus resembled that used by Horton and Davies for the investigation of the production of luminosity in atmospheric neon, and described in detail in their paper.† The present apparatus was fitted with two parallel lime-coated platinum filaments (only one of which was used at a time), in order to avoid delay when a filament burned through. The filaments, F, F, the gauze cylinder, G, and the anode, A, were enclosed, as shown in fig. 1, in a small glass vessel which could be arranged between the pole pieces, N and S,

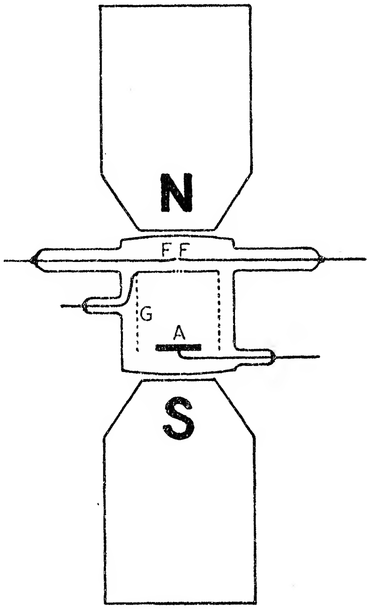

Fig. 1.

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* 'Phil. Mag.,' vol. 24, p. 746 (1921).

† F. Horton and A. C. Davies, 'Phil. Mag.,' vol. 41, p. 921 (1921).

of an electromagnet, which served to concentrate the luminosity into a bright column. By maintaining G and A at the same potential, and controlling the energy of the bombarding electrons by means of a potential difference applied between F and G, it was arranged that these electrons suffered no change of velocity throughout the space viewed by the spectroscope, except that resulting from collisions with helium atoms. The apparatus was arranged so that the lengths of the filaments were at right angles to the plane of the slit of the spectroscope. In this way the maximum concentration of luminosity was obtained in line with the axis of the collimator.

A modification of this form of apparatus was tried, in which both ends of the cylindrical gauze electrode were closed by platinum discs with gauze-covered central holes, and in which the anode, A, was replaced by a second lime-coated platinum filament, arranged 2 mm. below the bottom disc, parallel to the first filament, and in line with this and with the gauze-covered holes. It was anticipated that the simultaneous supply of electrons from opposite directions might facilitate the occurrence of multiple electron impacts, but in practice it was found to be of no advantage, and the form of apparatus finally adopted was that shown in fig. 1.

In the apparatus designed for the investigation of low voltage arcs a filament of fine tungsten wire was employed to supply the bombarding electrons. The apparatus was fitted with three such filaments, so as to avoid delay when one of them burned through. Fig. 2 shows the arrangement of the electrodes which was found to be most suitable, the section being in a plane at right angles to the lengths of the filaments, which were parallel to one another. The three filaments, F_1, F_2, and F_3, were sealed, as shown, into a spherical glass bulb of about 3·5 cm. radius. The anode, A, was a hollow platinum sphere, 1 cm. in diameter, rigidly attached by a stout platinum wire,

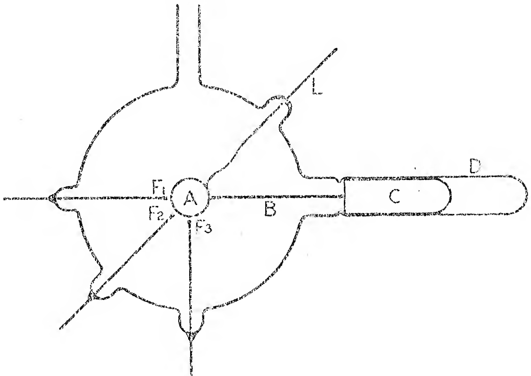

Fig. 2.

B, to the soft-iron piece, C. The wire, L, was connected with the sphere by means of a strip of platinum foil, about 2 mm. wide. The soft-iron piece fitted loosely into the side tube, D, of the enclosing glass bulb, and by means of an electromagnet it could be moved to different parts of this tube, thereby enabling the distance of the anode from the filaments to be varied over a range of about 2 cm. A limit to the forward motion of the anode was provided by a constriction in the tube D, which just prevented it from touching the filament F_1.

The method used for freeing the helium from hydrogen, and the arrangement employed for admitting the helium to the apparatus, were similar to those described elsewhere.* Both forms of apparatus were connected independently by side tubes with the carbon purifying tube through which the helium entered, and another tube from the arcing apparatus led through a stopcock and a second U-tube, immersed in liquid air, to the pumps and pressure gauge. The usual precautions were taken for ridding the glass walls and the electrodes of occluded gases.

A Hilger wave-length spectrometer was employed for the examination of the spectrum, and voltages were read on a high resistance voltmeter connected to the negative end of the filament and to the anode. The first appearance of the different lines, as the energy of the electrons was gradually increased, was investigated both visually and photographically. In order to investigate any connection that might exist between discontinuities in the current-potential difference curves and the appearance of a new line, or group of lines, in the spectrum, the current between the electrodes was measured at the same time as the visual observations of the spectrum were made.

The E.M.F. in the circuit was supplied by a 110-volts storage battery, the potential difference across the discharge tube, and the current through it, being regulated by means of series and parallel resistances. The current between the electrodes was read on a Weston milliammeter, provided with shunts, which was placed in series with the discharge tube. In investigating the minimum voltages at which the helium series lines could be stimulated, a potentiometer arrangement, by means of which the potential difference across the discharge tube could be varied in steps of one-tenth of a volt, was employed.

The potential differences measured on the voltmeter were all subject to a correction, to allow for the velocity of emission of electrons from the filament, etc. This correction was estimated in each case from the position of the ionisation bend in the current-voltage curves, and it has been taken into consideration in the curves given, and in the critical values stated.

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* 'Phil. Mag.,' vol. 42, p. 746 (1921).

During the observations, the carbon tube through which the helium was admitted to the apparatus was immersed in liquid air. In spite of the precautions taken to secure the purity of the helium used in these experiments, the presence of certain spectrum lines, other than those belonging to helium, was detected on some occasions. No lines were, however, detected, visually or photographically, before the helium lines appeared. The most persistent of the impurity lines was the hydrogen line H_β, and this was nearly always observed when the band lines were present. It seems probable that the hydrogen originated from the bombardment of the glass walls and metal parts of the apparatus, for, when the apparatus shown in fig. 1 was used, it was found that an intense glow was sometimes obtained, between the back of the filament and the upper glass wall of the apparatus, in the spectrum of which H_β could be seen clearly. Moreover, H_β could then be seen in the spectrum of the luminosity in any part of the column, even though no sign of its presence was obtained in an equally intense glow before the discharge passed to the walls.

At the highest pressures used, it was sometimes observed that certain of the bright lines in the red and orange, which were present when the helium band spectrum was very intense, appeared to coincide in position with certain of the brightest neon spectrum lines. The results obtained in these exceptional cases were, however, identical with those obtained in the absence of these lines. Under rather special circumstances, the mercury line λ 5461 was observed. The particular circumstances are given in detail later in the paper.

The Excitation Voltages for the Lines of the Orthohelium and Parhelium Series under Different Conditions.

The values of the minimum voltage at which lines of the orthohelium and parhelium series were first seen as the potential difference was gradually increased, and the stage at which they disappeared as the voltage was backed, varied very considerably in different experiments. There were, however, two limiting values, namely, 25·2 volts, the ionising voltage, and 20·4 volts, the minimum radiation voltage, which were associated with the excitation of these lines under different conditions. For moderate values of the intensity of the electron stream, and a gas pressure of about 1 mm. or less, the lines made their first appearance as, or after, the electron energy reached 25·2 volts, and disappeared, as the voltage was backed, at the same limit. For pressures above about 10 mm., and for intense electron streams, the lines appeared at 20·4 volts, or at some voltage between 20·4 and 25·2, and disappeared, as the voltage was backed, at 20·4 volts. In some of these cases the lines could be maintained, after having once appeared, at potential differences of about 13 volts. In such cases it was not possible to go on reducing the voltage until the lines vanished at some potential difference still lower, because the voltage eventually reached a value after which all attempts to reduce it still further resulted in an increase of potential difference. There was also a stage intermediate to those already mentioned, and which occurred under conditions of pressure and electron emission intermediate to those given above, when the lines appeared for increasing electron energies, at 25·2 volts, but vanished as the voltage was backed, at some voltage between 25·2 and 20·4.

The pressures which have been given as dividing results of one class from those of another are, however, only approximate, for it frequently happened that the change in the limit for the appearance or disappearance of lines could be effected by means of the heating current alone.

In many instances the lines of the orthohelium and parhelium series made their appearance very suddenly, and all together, as the energy of the bombarding electrons was increased, and there was a simultaneous discontinuity in the current-voltage curve, signifying a marked increase of current. In other instances the lines were seen very faintly at first, and then they gradually grew brighter as the electron energy was further increased. On these occasions, the yellow line, λ 5876, contrary to the predictions of Table II, was generally seen about one-tenth of a volt before the green line, λ 5016, which in turn appeared about one-tenth of a volt before the other lines. In certain instances the lines faded gradually as the voltage was backed, and did not all entirely disappear until 20·4 volts, there being no marked discontinuity in the current-voltage relations accompanying their disappearance. In these cases, λ 5876 and λ 5016 remained visible for one- or two-tenths of a volt after the other lines had vanished.

It has been shown in the introduction that there seems reason for the view that the orthohelium and parhelium principal series originate from the orbits to which an electron in a helium atom is removed as the result of 20·4 volts and 21·2-volts electron impacts, respectively. On this view, the values given in Table I are the minimum voltages at which the different lines could possibly be excited as the result of single electron impacts. Any limitation of possible electron displacements, such as that which is the basis of Table II, results in higher voltages than the corresponding values in Table I being required for the excitation of the various subordinate series lines of both systems. Since all the voltages given in Table I are greater than 23 volts, it follows that when lines of the helium spectrum are detected at about 20·4 volts, their presence cannot be due to the displacements of electrons within the atoms by single electron impacts. They must therefore be due to the cumulative effects of two or more electron impacts, and such cumulative effects would produce ionisation. Since the order of disappearance of the lines in this case (when ionisation is known to be occurring) is the converse of the order of their appearance as the potential difference is gradually increased, it is concluded that the detection of λ 5876 and λ 5016 before the other lines, in a few instances, is due to the fact that these lines are two of the brightest in the visible spectrum of helium at low voltages, and that it does not indicate any difference in the energy required for the excitation of different lines. The results thus indicate that the occurrence of ionisation of the helium atom is essential for the production of any of the orthohelium or parhelium lines.

Whenever members of the orthohelium and parhelium series are observed below 25·2 volts, ionisation of the helium by cumulative effects must thus be occurring. The current-voltage curves in these cases show a marked discontinuity, indicating an abrupt increase of current, either simultaneously with, or shortly after, the first appearance of spectrum lines. This discontinuity is presumably caused by the increase of electron current which results from neutralisation of the space charge of the emitted electrons by the positive ions produced by ionisation of the helium. The increase in the electron current increases the ionisation by cumulative effects very considerably, and hence the spectrum lines can be *maintained* while the voltage is backed below 25·2 volts, in cases when they cannot be *excited* below this value.

When the lines were maintained below 20·4 volts, and the stage below which the voltage could not be further reduced, was passed, the relative intensities of the different series lines at the same potential difference before and after the minimum value were not the same. This is shown by the two last columns of Table III. The first and second columns give the wavelength and the series of the observed orthohelium and parhelium series lines, and the third column gives their intensities (as judged from visual observations) at 19·0 volts, before the minimum value of the voltage was reached. The fourth column of the Table gives the intensities of the same lines at 19·0 volts, after the minimum value was passed. Lines of the orthohelium and parhelium series further in the violet than λ 4472 could not be seen in either case and a photographic comparison of this part of the spectrum in the two cases could not be made because, owing to the high temperature at which the filament had to be maintained in order to attain a potential difference of

19·0 volts after passing the minimum value, the discharge could not be left running continuously for the time of exposure necessary to obtain a photograph.

Table III.

Wave-length.	Series.	Intensity before the minimum voltage.	Intensity after the minimum voltage.
7066	2, $p-m$, s	5	1
6678	2, $\mathrm{P}-m$, D	15	3
5876	2, $p-m$, d	20	8
5048	2, $\mathrm{P}-m$, S	3	3
5016	2, $\mathrm{S}-m$, P	15	4
4922	2, $\mathrm{P}-m$, D	10	0·5
4713	2. $p-m$, s	10	0·5
4472	2, $p-m$, d	15	3

Since the lowest potential difference at which the orthohelium and parhelium series lines were ever excited (as distinct from maintained) was 20·4 volts, the maintenance of the lines below this value must be due to the presence of atoms which are in an abnormal (more easily ionisable) condition. The number of atoms which are in this condition must remain constant, for no new ions or abnormal atoms can be produced from normal helium by electron bombardment below 20·4 volts, and the fact that the luminous discharge was maintained for long periods at voltages below 20·4, shows that there was no gradual reduction in the number of ionisable atoms present. Therefore, when the lines are maintained at low voltages, the frequency of electron collisions with helium atoms must be such that, on recombination occurring, the returning electron is unable to fall right back to the normal orbit before being again ejected by another impact.* The current through the discharge tube must in these cases be carried entirely by electrons, for if any of it were carried by helium positive ions the number of these would diminish with time and the glow would not be maintained. The electron current measured in these circumstances is not, however, the value of the electron emission which would normally be obtained for the given values of the heating current and the voltage, because the positive ions present influence the space charge of the emitted electrons. The variation in the extent to which the space charge is influenced with increase of the heating current, and with increase of the series resistance, accounts for the variation in the current-voltage relations with these factors, and also for the reversible character of the changes.

About 13 volts was the minimum value of the potential difference at which lines of the orthohelium and of the parhelium series were maintained in the present research, but there seems to be no reason for regarding this value as a definite minimum potential difference at which it is possible to maintain them.

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* It follows on this view that when the spectrum is maintained below 20·4 volts none of the extreme ultra-violet series lines of helium can be present.

Examples of current-voltage curves are given in figs. 3 and 4 and in fig. 5. The continuous curve in each case gives the variations of the current as the voltage was gradually increased, and the curve drawn with a broken line gives the corresponding values of the current as the adjustments were made in the

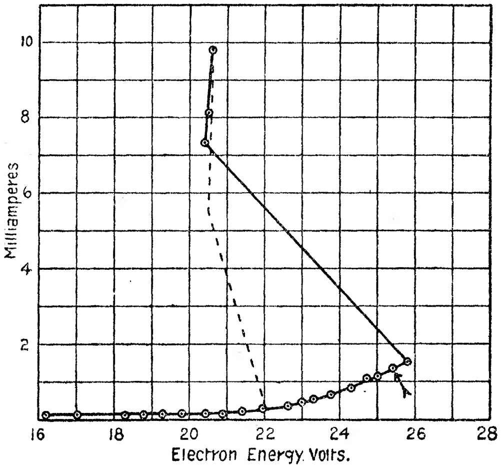


Fig. 3.

The arrow indicates the point at which lines of the orthohelium and parhelium series first appeared.

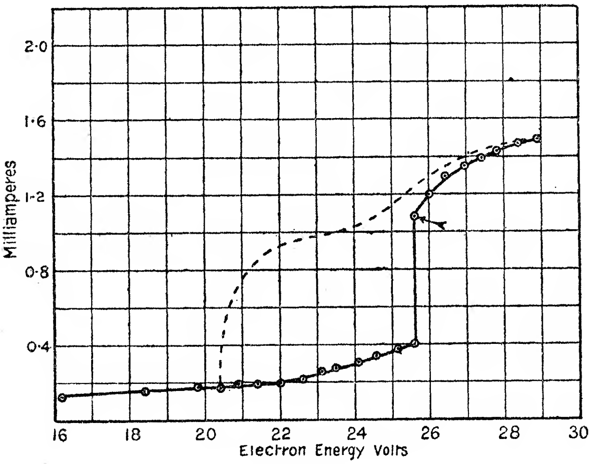


Fig. 4.

The arrow indicates the point at which lines of the orthohelium and parhelium series first appeared.

reverse order. The series of observations recorded in figs. 4 and 5 were taken at the same pressure, 19 mm., but the filament temperature was much higher for the series recorded in fig. 5 than for that recorded in fig. 4. The pressure during the observations of fig. 3 was 25 mm. These three curves all show a marked discontinuity at, or near, the voltage at which lines were first detected.

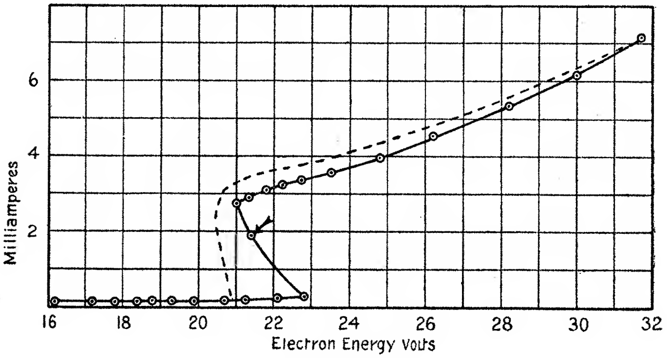


FIG. 5.

The arrow indicates the point at which lines of the orthohelium and parhelium series first appeared.

The Minimum Excitation Voltage for the Line λ 4686 *of the Enhanced Series, under Different Conditions.*

Under different sets of conditions, three distinct limits were found for the minimum voltage at which λ 4686 could be obtained. These limits are the three critical voltages 80·0, 54·2, and 50·8, mentioned in connection with this line in the introduction. About 80 volts was the limit at which λ 4686 could be detected visually or photographically when the pressure of helium was 1 or 2 mm. At pressures rather greater than this, 80 volts was the limiting value only when the electron current density was not too high. With intense electron streams at these pressures, λ 4686 could be detected down to a voltage of about 54. Whenever λ 4686 was seen in the neighbourhood of 54 volts, the lines of the helium band spectrum were always visible, whereas in the circumstances in which 80 volts was obtained as a lower limit, the band spectrum was faint, and in some instances was definitely absent. The photographs 1 and 2 of Plate 13 illustrate this difference in the appearance of the spectrum in the two cases. Both of these were taken using the apparatus of fig. 1. In the case of the first photograph, the voltage across the discharge tube was 96, and the current varied from 2 to 5 milliampères during the exposure. λ 4686 could not be seen below 80 volts under these conditions. In the case of photograph 2, the voltage varied from 55 to 60 during the exposure of the plate, and the current across the discharge tube varied from 25 to 30 milliampères. The line λ 4686 can be detected in both of these photographs, though in 2 it is not quite so plain as in 1 owing to the presence of the band lines.

The difference in these two photographs corresponds to a definite difference in the current-voltage conditions with respect to a discontinuity in the current-voltage curve, which can best be explained by reference to the curve given in fig. 6. This curve, which is a continuation of a curve corresponding to a series of observations identical with that represented by the continuous curve in fig. 5, shows a discontinuity between 44 and 45 volts. At this discontinuity the helium band spectrum appeared, and there was a marked change in the appearance of the luminosity, the glow assuming the form of a brilliant arc and becoming more purple in colour. The orthohelium and parhelium series lines made their appearance simultaneously with the occurrence of the discontinuity between 22 and 23 volts, shown in fig. 5. The increase in the current through the discharge tube, and the decrease in the potential difference across it, were sometimes even more marked than in the case given in fig. 6. The voltage at which the second discontinuity occurred did not have any fixed value but depended upon the pressure of helium and upon the intensity of the electron stream, being higher at low pressures and for less intense bombarding streams. At the highest pressures used, *i.e.*, from about 25 to 36 mm., it occurred at the same voltage as the first discontinuity, and the line spectrum and the band spectrum of helium made their appearance together. Photograph 1 was taken when only a small second discontinuity had occurred, while photograph 2 was taken after the occurrence of a marked discontinuity.

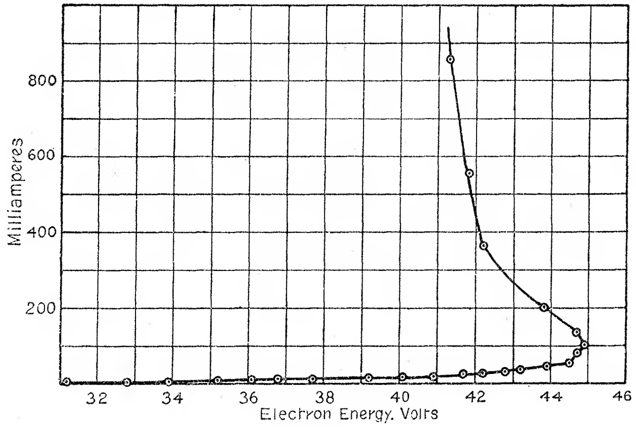
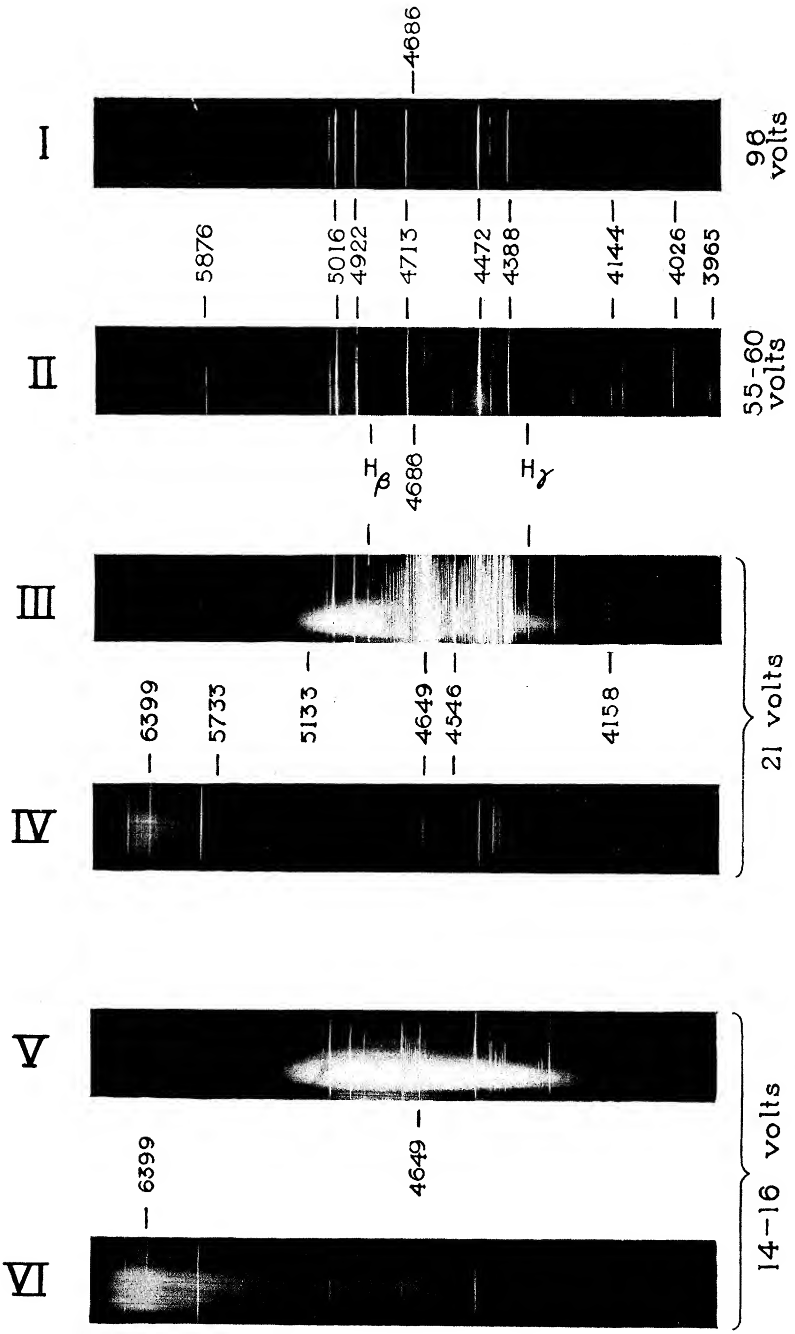


Fig. 6.


4686
I
98 volts
5876
5016
4922
4713
4472
4388
4144
4026
3965
II
55-60 volts
Hβ
4686
Hγ
III
5133
4649
4546
4158
21 volts
6399
5733
IV
V
4649
6399
14–16 volts
VI

In a large number of visual observations under conditions somewhat similar to those in which photograph 2 was taken, the voltage at which λ 4686 was first seen to stand out from among the band lines was between 54 volts and 55 volts, indicating a limit at the critical voltage for the further ionisation of the helium positive ion. At still higher pressures and with intense electron streams, λ 4686 could first be seen to stand out from the band spectrum lines when the potential difference across the discharge tube was adjusted to about 51 volts. In these cases the band spectrum was more intense relatively to the orthohelium and parhelium series lines than in photograph 2. It was found, however, that for both increasing and decreasing adjustments of the potential difference, λ 4686 could be seen to stand out distinctly from the band lines when the voltage was above 50·8. Attempts to see λ 4686 below this voltage were unsuccessful.

At pressures from about 20 mm. to 36 mm., the highest pressure used, it was only possible to raise the potential difference across the discharge tube above about 40 volts when the electron current density was too low to cause a second discontinuity in the current voltage relations to occur, and at these pressures the enhanced line λ 4686 was not seen at all. This result is in accord with that of Compton, Lilly, and Olmstead (*loc. cit.*) who failed to excite the enhanced lines at any voltage used with pressures above 10 mm.

If 50·8 volts is a genuine limit for the excitation of λ 4686, it may be concluded that the line can be stimulated without further ionisation of the helium positive ion. If, however, λ 4686 can be obtained at voltages below 50·8, this conclusion is not justified. It has been shown in the case of the lines of the orthohelium and the parhelium series that these can be excited at voltages intermediate to the ionisation voltage, 25·2, and the minimum radiation voltage, 20·4, this latter value being a limit for their excitation. The corresponding theoretical value in the case of the enhanced lines is 40·6 volts, which corresponds to the energy necessary to produce the fundamental displacement of the remaining electron in an already ionised helium atom, *i.e.*, it is the voltage corresponding to the radiation whose frequency is given by $\nu = 4N(1/1^2 - 1/2^2)$. Therefore, if λ 4686 could be excited at voltages between 50·8 and 40·6, it would follow that further ionisation of already ionised helium atoms was occurring as the result of cumulative effects. It has already been stated that no evidence of the presence of λ 4686 below 50·8 volts was obtained; the results of the present research therefore indicate that the detection of λ4686 between 54 volts and 50·8 volts does not result from the removal of the remaining electron in a positively charged helium atom as the result of cumulative effects, but from single electron impacts on helium positive ions without the occurrence of further ionisation.

The Minimum Excitation Voltage for the Lines of the Helium Band Spectrum.

Reference has already been made in the last section to the prominence of the band spectrum of helium after the occurrence of a second marked discontinuity in the current-voltage relations. A more complete account of the conditions under which the band spectrum was seen is given in the present section. The general indications were that it was not present at all until a second discontinuity had taken place. The abrupt increase of current, and the simultaneous fall in the potential difference, which constitute the discontinuity, could be brought about by gradually increasing the temperature of the filament, if the voltage across the tube were sufficiently high.

The value of the voltage after the discontinuity, could be varied to a certain extent by varying the filament temperature, the series and parallel resistances, and the E.M.F. in the circuit, though at each pressure there was a limit below which it could not be reduced. Increase of the E.M.F. in the circuit after this limit had been reached merely increased the current through the discharge without altering the potential difference across it. The limiting value of the final potential difference after the discontinuity depended upon the distance apart of the electrodes and upon the form of the apparatus; for any given form it decreased as the pressure of helium increased. In the case of the apparatus shown in fig. 2, it was found that the lowest limit was obtained when the anode was 2 mm. from the filament. In the present research, about 13 volts was the lowest value obtained, and this occurred when using the apparatus of fig. 2 with helium at about 30 mm. pressure.

Lines of the helium band spectrum could always be seen at the final potential difference after the discontinuity, so that the voltage limit for its detection varied with the pressure of helium in the same way as the limit for this final potential difference varied. The minimum initial voltage at which the changes could be made to take place, and at which the helium band spectrum was first seen (*i.e.*, the minimum voltage just before the occurrence of the discontinuity in the current-voltage relations), was the minimum radiation voltage 20·4. At high pressures the band spectrum and the orthohelium and parhelium series lines appeared simultaneously at this voltage. The band spectrum was never in any circumstances seen without the orthohelium and the parhelium series lines being seen also, though at the higher pressures it was relatively more intense with respect to these lines than at lower pressures.

The presence of the helium band spectrum at low voltages is shown in photographs 3, 4, 5 and 6. Nos. 3 and 5 were taken on a Wellington-Speedy plate, the time of exposure being 65 minutes for 3 and 80 minutes for 5. Nos. 4

and 6 were taken under conditions which were identical with those for Nos. 3 and 5 respectively, but on a Wratten panchromatic plate, the times of exposure being the same as for 3 and 5 respectively. The potential difference across the discharge tube for the photographs 3 and 4 was 21 volts, and for photographs 5 and 6 it was 14 volts, with an occasional fluctuation up to 16 volts. An immediate readjustment to 14 volts was made every time a fluctuation occurred.

In the band spectrum obtained in the experiments referred to in this section, the first doublet of the main series, and the first doublet of the second series, discovered by Fowler,* were identified visually. The heads in the first main series doublet are at λ 4625·4 and λ 4648·5, and the heads in the first doublet of the second series are at λ 5133·3 and λ 5108·2. The details of the first main series doublet, given by Fowler, were clearly recognisable visually, and can be seen in photograph 3. In addition to these doublets, the prominent single-headed fluting at λ 5733, degrading towards the violet, recorded by Curtis† and by Fowler, was seen. All the heads down to λ 4546, recorded by Curtis, were also observed visually. Of these, the heads at λ 5733 and λ 6399 were the most prominent. These are present in photograph 4. When the external conditions controlling the discharge were varied in such a way as to make the band spectrum fade in brightness, λ 5733 was one of the last lines to disappear, as judged from visual observations.

The results stated in this section show that the only limit which can be definitely associated with the helium band spectrum is the minimum radiation voltage, 20·4, and that this is only associated with it in that it has not been found possible *to excite* (as distinct from *to maintain*) the band spectrum of helium below this voltage. The view that the systems which give rise to the helium band spectrum are molecules formed by the combination of abnormal helium atoms, obtains support from the fact that the band spectrum was never observed in the absence of the orthohelium and parhelium series spectrum, and from the variation in the relative intensities of these two spectra with variation of the pressure of the helium. No evidence is afforded, however, as to the particular nature of the abnormal helium atoms concerned.

It follows from the above view that, when the band spectrum of helium is maintained below 20·4 volts, the number of helium molecules present cannot be increased without causing a reduction in the number of abnormal atoms present. The band spectrum of helium, like the series lines, has been maintained for prolonged periods below 20·4 volts, so that the number of molecules which are capable of giving rise to the band spectrum at these voltages, whether they are normal molecules, or molecules maintained in some abnormal condition, must remain constant in these circumstances.

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* A. Fowler, 'Roy. Soc. Proc.,' A, vol. 91, p. 208 (1915).

† W. E. Curtis, 'Roy. Soc. Proc.,' A, vol. 89, p. 146 (1913).

Though the helium band spectrum was maintained down to the same limit as the orthohelium and parhelium series lines, it was not present in the spectrum of the discharge when the minimum voltage in the current-voltage relations had been passed, and the potential difference was increasing again in spite of all attempts to reduce it still further. As the voltage was being gradually reduced to the minimum value, both the series lines and the band spectrum diminished in intensity, the latter at a more rapid rate than the former. Sometimes only the heads of the bands, and not the detail, could be seen when the minimum value was reached. After passing the minimum value of the potential difference, the band spectrum had completely disappeared and the mercury line λ 5461 stood out clearly, although it was much fainter than the brightest lines of the orthohelium and parhelium series.* On further increasing the voltage, the line increased in intensity, reached a maximum brightness, and ultimately faded out entirely. The hydrogen line H_β, like the helium band lines, was not visible after passing the minimum value of the potential difference.

The changes in the spectrum, like the changes in the current-voltage relations which occur simultaneously, were found to be reversible, and after re-passing the minimum voltage on effecting the current-voltage changes in the reverse order, the helium band spectrum reappeared and the mercury line vanished. The disappearance of the band spectrum without the disappearance of the series lines, when the voltage was varied by altering the heating current, or the series resistance, and its subsequent reappearance when the variations of the controlling factor were made in the opposite order, admit of explanation in two ways.

The first explanation is analogous to the explanation of the maintenance of the series lines below 20·4 volts, by the presence of atoms maintained in an abnormal, more easily ionisable, condition, by the frequency of electronic-atomic encounters. It is possible that a somewhat similar effect occurs in the case of the helium molecules and that these, under intense electron bombardment, when no new molecules can be produced, are maintained in such a state of excitation that they are prevented from emitting the part of the band spectrum which falls in the region of the spectrum investigated.*

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* It must be remembered that the carbon purifying tube attached to the discharge tube was immersed in liquid air during the experiment, so that the amount of mercury vapour present must have been very minute.

The second possible explanation involves the assumption that a particular type of abnormal helium atom is essential for the production of the helium molecule, and that the constancy of the supply of molecules at any given values of the heating current and the voltage (below 20·4 volts) is maintained by the dissociation of a certain number of molecules into abnormal atoms and the formation of an equal number of new molecules. Clearly, in this case, the supply of molecules would decrease when the frequency of electron encounters with helium atoms reduced the supply of the particular type of abnormal atom required; hence the band spectrum would fade and eventually disappear, though it might reappear on reducing the electron bombardment. If this explanation is correct, one or more series of lines of the orthohelium and parhelium systems must disappear when the band spectrum disappears. Table III shows that none of the lines between λ 7066 and λ 4472 disappear under these circumstances, so that the series must be one having no lines within this region. The orthohelium principal series is the only series which fulfils this condition, and this is the one which results from transitions involving a return of the displaced electron to the 20·4 volts orbit. If the disappearance of this series at the same time as the helium band spectrum could be proved, evidence would be obtained not only in favour of the second explanation offered above, but also of Franck and Knipping's suggestion as to the nature of the helium molecule.

Conclusion.

It has been shown in the course of the foregoing pages that none of the orthohelium and parhelium lines can be excited without all of them being stimulated, and that the ionisation of the atom is essential for their production. With the exception of this fact, all the results of the present investigation, in so far as it is concerned with these lines and with the line λ 4686 of the enhanced series, are in accord with Bohr's theory of radiation. The necessity for the occurrence of ionisation before the emission of the orthohelium and parhelium series lines can take place seems, however, to indicate some limitation of those electron transitions within the helium atom which involve an increase in the potential energy of the atomic system, not predicted by Bohr's theory. The limitation indicated is one which prevents direct transitions within the atom from the normal orbit to any orbits of either the crossed system, or the coplanar system, except the 2, S and the 2, *s* orbits.

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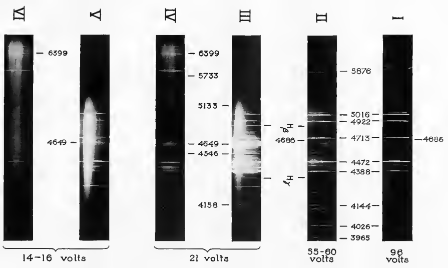
* The disappearance of H_β could be explained in a similar way, and it seems possible that the appearance of the mercury line λ 5461, for a short stage in the current-voltage relations, may be another manifestation of a similar occurrence.

The results of the present investigation are thus directly opposed to the conclusion drawn by Franck and Knipping that the bends in their current-voltage curves in helium between 21·2 volts and 25·2 volts are due to the excitation of successive lines of an ultra-violet series, by the return of the electron after displacement to successive outer orbits of the helium atom. On the other hand, the results of the present investigation of normal uncharged helium are in complete agreement with the results of the investigations of McLennan and Ireton on the vapours of zinc, cadmium, and mercury, and of Foote and Meggers on cæsium vapour.

The excitation of λ 4686 at voltages above 50·8 volts, and not below this value, indicates that a similar limitation does not hold in the case of the stimulation of this line from a helium positive ion. It would be of interest to ascertain whether such a difference between neutral and ionised atoms occurs in other cases, for instance in mercury, zinc, or cadmium, vapour.

The conditions under which the band spectrum of helium made its appearance, and those under which it could be maintained, support the view that this spectrum has its origin in a helium molecule which is produced from abnormal helium atoms, and thus that it cannot be produced in normal helium for electron energies below 20·4 volts. The results of the present research afford no information regarding the energy which is necessary in order to excite the molecule to the emission of the band spectrum, beyond the fact that this energy can be acquired, under intense electron bombardment, at a potential difference of 20·4 volts. The results of the present investigation, however, considered in conjunction with the recent conclusions of Horton and Davies, namely, that at 20·4 volts some system is produced in helium which can be ionised by the radiation produced at 21·2 volts, support the suggestion made by Franck and Knipping that the coplanar atoms resulting from 20·4 volts electron collisions with helium atoms are capable of forming He_2 molecules, which give rise to the band spectrum.

In conclusion, I wish to express my best thanks to Prof. F. Horton for his kind interest and advice during the course of this investigation.


VI
V
IV
III
II
I
6399
4649
6399
5733
5133
4649
4546
4158
Hβ
4686
Hγ
5876
5016
4922
4713
4472
4388
4144
4026
3965
4686
14-16 volts
21 volts
55-60 volts
96 volts